

# PATENT SPECIFICATION

NO DRAWINGS

*Inventors:* OSKAR RIESTER, JUSTUS DANHAUSER, HANS OHLSCHLAGER,  
ECKART SEELIG and WILLIBALD PELZ

1.150.987



1.150.987

Date of Application and filing Complete Specification: 27 April, 1967.  
No. 19435/67.

Application made in Germany (No. A52306 IXa/57b) on 29 April, 1966.  
Complete Specification Published: 7 May, 1969.

© Crown Copyright 1969.

Index at acceptance: —C3 P(4A, 4D1A, 4D3B1, 4K7, 4K10, 4T2A, 4T2D, 4T2X, 7A, 7D1A, 7K4, 7T2A, 7T2D, 7T2X, 10A, 10D1A, 10K4, 10T2A, 10T2D, 10T2X); C2 C(3C5A4, 3C5C7, 3C5E5); G2 C(C4B1D1B, C4B1DY, C4C5A, C4D3X, C14)

Int. Cl.: —C 08 f 15/02

## COMPLETE SPECIFICATION

### Sensitization of Light-Sensitive Polymers

We, AGFA-GEVAERT AKTIENGESellschaft, a body corporate organised under the laws of Germany of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

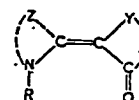
The present invention relates to the sensitization of light-sensitive polymers for use in photographic reproduction.

It is well known in the art of photomechanical reproduction that light-sensitive polymers may be used to form resist images. These polymers are applied as a thin layer to a suitable support, and, after exposure, may be selectively dissolved out in the unexposed areas by development with a solvent, while the exposed and changed image parts of the layer remain insoluble in the solvent. These light-sensitive synthetic resins contain light-sensitive groups such as cinnamic acid, azido, or sulphazido groups.

It is also known that the light-sensitivity of these synthetic resins can be greatly enhanced by using such sensitizers as triphenylmethane dyes, aromatic ketones, or nitro compounds.

An object of the present invention is to provide new sensitizers and to increase, as much as possible, the light-sensitivity of synthetic resins which undergo cross-linking on exposure to light.

We now have found that the light-sensitivity of film-forming polymers of copolymers which undergo cross-linking upon exposure to light, can be greatly increased by incorporating therein a sensitizer of the following formula:



wherein

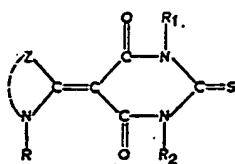
Z represents the ring members necessary for completing a thiazole, benzothiazole, naphthothiazole, selenazole, benzoselenazole or naphthoselenazole ring, Y represents the ring members necessary for completing a thio-barbituric acid ring and

R represents an alkyl radical containing preferably up to 5 carbon atoms, an aryl radical preferably phenyl or an aralkyl radical preferably benzyl or phenyl-ethyl, or an alkyl radical containing preferably up to 5 carbon atoms which is substituted by at least one of the following substituents: carbonyl, sulphonyl, sulphoamide, sulphate or phosphoric acid.

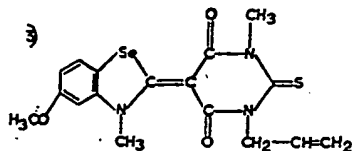
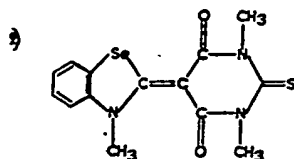
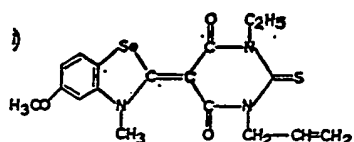
The heterocyclic rings or aryl groups fused thereto, contained in the compound of the above formula may be further substituted in any way desired, e.g. by alkyl groups containing preferably up to 5 carbon atoms, such as methyl or ethyl, halogen atoms such as chloride or bromine, alkoxy groups containing preferably up to 5 carbon atoms, such as methoxy or ethoxy, hydroxyalkyl or thioalkyl groups, aryl groups such as phenyl, aralkyl groups such as benzyl, or amino or substituted amino groups.

The nature of these substituents is of secondary importance in relation to the sensitizing effect. However, by suitable choice of substituents, other physical properties such as solubility can be influenced as required. Pre-

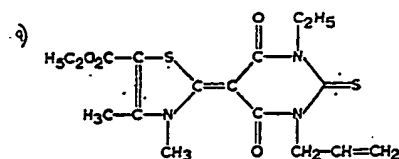
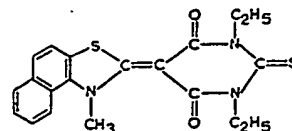
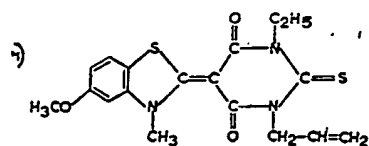
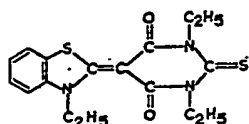
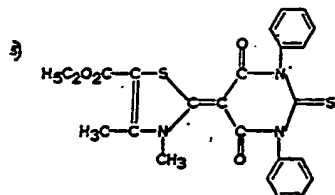
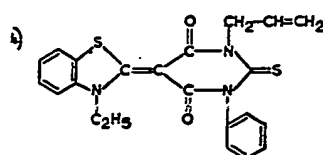
ferred compounds are those compounds which are of the following formula



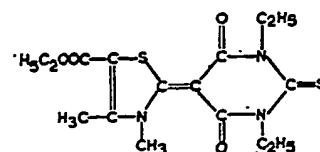
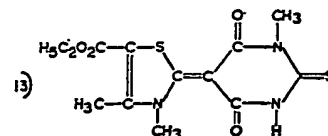
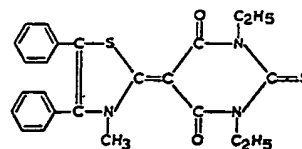
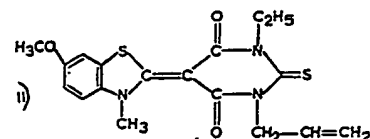
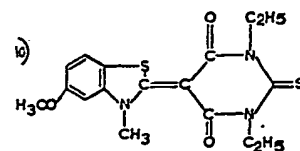
- 5 wherein Z and R have the meanings indicated above and R<sub>1</sub> and/or R<sub>2</sub> represents a hydrogen atom, an alkyl radical having up to 5 carbon atoms such as methyl or ethyl, or an olefinically unsaturated aliphatic radical having up to 5 carbon atoms such as allyl or phenyl.
- 10 Particularly suitable are, for example, compounds of the following formulae:



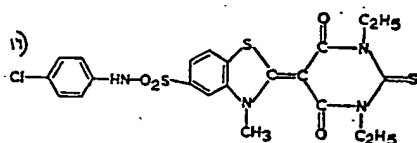
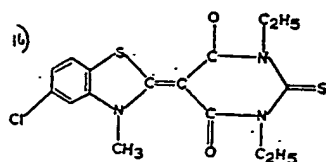
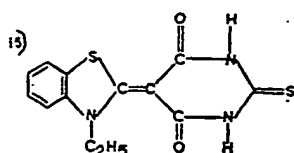
15



20



25



5 The sensitizers to be used in the present invention can be prepared by conventional methods, for example, by condensation of a methyl mercapto quaternary salt of a heterocyclic base with a ketomethylene compound in pyridine or in alcohol, with the addition of a base such as triethylamine.

10 The preparation of sensitizer 6 is described in detail below:

#### Sensitizer 6

15 3.5 g of N - ethyl - 2 - methylmercapto - benzothiazolium - ethyl sulphate were heated on a steam bath for 15 minutes with 2 g. of 1,3 - diethyl - thiobarbituric acid in 20 cc. of pyridine. The solution was poured into ice water and the resulting pale yellow precipitate was filtered under suction and recrystallised twice from methanol. M.p. 161—163° C.

20 The sensitizers used in the present invention increase the light-sensitivity of film-forming polymers which undergo cross-linking on exposure to light. They are preferably used in combination with light-sensitive polymers or copolymers in which the groups capable of cross-linking under the influence of light are cinnamic acid or azido groups. Polymers of this type, and light-sensitive layers produced therefrom have been described, for example, in British Patent Specifications Nos. 695,197 and 822,861.

25 Polymers containing azido groups are described in British Patent Specifications Nos. 843,542, 843,541 and 815,471. Polymers containing sulphazide groups are described in German Patent Specification No. 1,224,494 and Belgium Patent Specifications Nos. 665,427 and 645,428.

Further suitable light-sensitive polymers are described in French Patent No. 1,475,296.

The sensitizers according to the invention are employed in the usual manner. The light-sensitive synthetic polymers are dissolved in suitable solvents, and the sensitizer is added to the casting solution.

The concentration of sensitizer in the light-sensitive layer is not critical and depends somewhat upon the solubility of the sensitizing agent in the particular solvent used for the light-sensitive polymer in the final layer. The required concentration depends furthermore on the original sensitivity of the light-sensitive polymer and to some extent on the thickness of the final layer, in that it will vary according to the slightly lower concentration usually employed in the case of thicker layers in order to ensure thorough hardening of the layer.

The optimum concentration can be determined in known manner by a few simple tests customarily employed in the art. A concentration of 0.5 to 10%, preferably 1 to 7% by weight, based on the weight of the light-sensitive layer is usually sufficient.

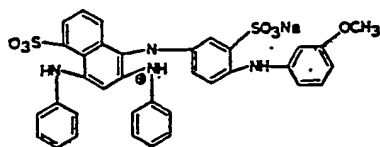
The sensitized layers of the present invention are processed in accordance with common practice. The source of light employed is preferably a high-energy carbon arc lamp or a mercury vapour lamp. After exposure, the layer is developed in known manner by dissolving out the unexposed parts of the layer. Suitable solvents and solvent concentrations for the coating compositions and for developing the exposed sensitive layers of the invention can be selected from those set forth in the patent specifications mentioned hereinbefore. The relief images obtained can then be used in the usual ways.

In order that the invention may be more fully understood, the following Examples in which all parts and percentages are based on weight, are given by way of illustration only:—

#### EXAMPLE 1

4 g. of a reaction product of 1 part of ethylene-vinyl alcohol copolymer and 2 parts of *m* - isocyanato - cinnamic acid ethyl ester (see British Patent Specification No. 822,861) and 0.04 g. of sensitizer No. 12 were dissolved in 46 g. butyl acetate. An aluminium foil was coated with the solution in a centrifuge (100 revolutions per minute) and was dried for 5 minutes.

The layer was exposed for 5 minutes behind a grey step wedge with a carbon arc lamp (30 A., 42 V.) at a distance of 70 cm, and was developed for 2 minutes in butyl acetate which contains 0.1% Irisolechtblau GLE (C.I. Solvent Blue 50) which is the amino-salt of the following compound (C.I. Acid Blue 102; C.I. 50320)



The layer was washed with water and dried in air. 9 steps of the grey wedge were visible on the support.

5 In the layer was exposed under the same conditions without the addition of sensitizer, then only 2 steps of the grey wedge were visible. Density of step 2: 0.17, step 9: 1.23. This corresponded to an 11.5-fold increase in sensitivity on the addition of sensitizer.

10 The increase in sensitivity obtained when other sensitizers according to the invention were used instead of sensitizer 12, are as shown in the following table:

15	Sensitizer No.	Relative sensitivity
	1	11.3
	2	11.3
	3	11.3
	4	11.3
20	5	11.3
	7	16.5
	8	17
	9	10
	10	11.7
25	11	16.5
	12	11.5
	14	17
	16	11.3
	17	16.5
30	Michler's ketone	7.5

The sensitivity of the sensitized layer compared with that of a non-sensitized layer is calculated from the number of coloured steps of the layer remaining on the support according to the equation:

$$S_x = \frac{\text{antilog } D_x}{\text{antilog } D_o}$$

40 where  $D_x$  is the density of the last step of the sensitized layer still adhering to the support, and  $D_o$  is the density of the last step of the non-sensitized layer still found on the support.

#### EXAMPLE 2:

45 The procedure carried out was the same as that described in Example 1, except that instead of the light-sensitive polymer used in Example 1, a polymer which had been obtained by reacting 10 g. of a copolymer of vinyl chloride and vinyl alcohol with 7.3 g. of p-azidobenzoyl chloride in pyridine (see also British Patent Specification No. 843,541) was used.

The increase of sensitivity is shown in the following table:

Sensitizer No.	Relative sensitivity	
6	35	55
8	35	
14	35	

#### EXAMPLE 3:

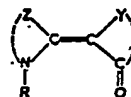
The procedure was performed in the manner described in Example 1. The light-sensitive polymer used was that indicated in Example 7 of German Patent No. 1,224,494.

The effect of the sensitizers according to the present invention is illustrated by the table below.

Sensitizer No.	Relative sensitivity	
1	3.5	
10	5.5	
11	4.6	
13	8	70
15	11.8	
16	8	

#### WHAT WE CLAIM IS:—

1. A light-sensitive photographic layer comprising a light-sensitive film-forming polymer or copolymer capable of being cross-linked upon exposure to light which layer contains a sensitizer of the following formula:



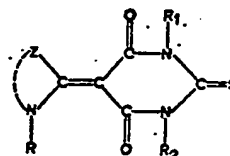
wherein

Z represents the ring members required to complete a thiazole, benzothiazole, naphthothiazole, selenazole, benzoselenazole or naphthoselenazole ring;

Y represents the ring members required to complete a thiobarbituric acid ring and

R represents an alkyl, aryl or aralkyl radical or an alkyl radical which is substituted by at least one of the following substituents: carboxyl, sulpho, sulphonamide, sulphate or a lid in the form of a spherical dome of which phosphoric acid.

2. A light-sensitive photographic layer comprising a light-sensitive film-forming polymer capable of being cross-linked upon exposure to light which layer contains a sensitizer of the following formula:



wherein

Z represents the ring members required to

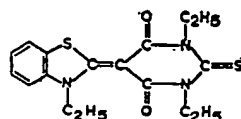
complete a thiazole, benzothiazole, naphthothiazole selenazole, benzoselenazole or naphthoselenazole ring;

- 5 R represents an alkyl radical containing up to 5 carbon atoms, a phenyl radical or an alkyl radical having up to 5 carbon atoms which is substituted by at least one of the following substituent carboxyl, sulphy, sulphonamide, sulphate or phosphoric acid;
- 10 R<sub>1</sub> and/or R<sub>2</sub> represents a hydrogen atom, an alkyl radical containing up to 5 carbon atoms, an olefinically unsaturated aliphatic radical containing up to 5 carbon atoms or a phenyl radical.

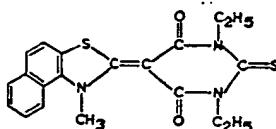
- 15 3. A light-sensitive layer as claimed in claim 1 or claim 2 in which the heterocyclic rings or aryl groups fused thereto in the sensitizer, are further substituted.

- 20 4. A light-sensitive photographic layer as claimed in any one of claims 1 to 3, wherein the groups capable of undergoing cross-linking upon exposure to light are cinnamic acid or azido or sulphazido groups.

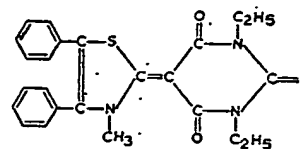
- 25 5. A light-sensitive photographic layer as claimed in claim 2, wherein the sensitizer has the following formula:



- 30 6. A light-sensitive photographic layer as claimed in claim 2, wherein the sensitizer has the following formula

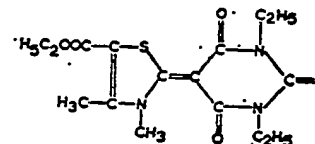


7. A light-sensitive photographic layer as claimed in claim 3, wherein the sensitizer has the following formula



35

8. A light-sensitive photographic layer as claimed in claim 3, wherein the sensitizer has the following formula:



9. A light-sensitive photographic layer as claimed in claim 1 wherein the sensitizer used is any one of the compounds 1 to 17 herein described. 40

10. A light sensitive photographic layer as claimed in any one of claims 1 to 9 containing the sensitizer compound in a concentration of 0.5 to 10% by weight based on the weight of the light-sensitive layer. 45

11. A light-sensitive photographic layer as claimed in claim 1 substantially as herein described with reference to the Examples. 50

ELKINGTON & FIFE,  
Chartered Patent Agents,  
High Holborn House, 52-54 High Holborn,  
London, W.C.1.  
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1969.

Published by the Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.